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Odor and Odorous Chemical Emissions from Animal Buildings: Part 1. Project Overview, Collection Methods, and Quality Control

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ODOR AND ODOROUS CHEMICAL EMISSIONS FROM ANIMAL BUILDINGS: PART 1. PROJECT OVERVIEW, COLLECTION METHODS, AND QUALITY CONTROL

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ABSTRACT. *Livestock facilities have historically generated public concerns due to their emissions of odorous air and various chemical pollutants. Odor emission factors and identification of principal odorous chemicals are needed to better understand the problem. Applications of odor emission factors include inputs to odor setback models, while chemical emission factors may be compared with regulation thresholds as a means of demonstrating potential health impacts. A companion study of the National Air Emissions Monitoring Study (NAEMS) included measurements necessary for establishing odor and chemical emission factors for confined animal feeding operations. This additional investigation was conducted by the University of Minnesota, Iowa State University, West Texas A&M Agri-Life Center, and Purdue University. The objectives were to (1) determine odor emission rates across swine and dairy facilities and seasons using common protocols and standardized olfactometry methods, (2) develop a chemical library of the most significant odorants, and (3) correlate the chemical library with the olfactometry results. This document describes the sampling and quality assurance methods used in the measurement and evaluation of odor and chemical samples collected at two freestall dairy farms, one sow (gestation/farrowing) facility, and one finishing pig site. Odor samples were collected in Tedlar bags and chemical samples were collected in sorbent tubes at barn inlet and exhaust locations using the NAEMS multiple-location gas sampling systems. Quality assurance protocols included interlaboratory comparison tests, which were evaluated to identify variations between olfactometry labs. While differences were observed, the variations among the labs and samples appeared random and the collected odor data were considered reliable at a 0.5% level of statistical significance. Overall, the study took advantage of groundbreaking opportunities to collect and associate simultaneous odor and chemical information from swine and dairy buildings while maintaining accordance with standard methods and comparability across laboratories.*

Keywords. *Animal feeding operation, Chemical, Dairy, Emission, Methods, Odor, Swine.*

Livestock facilities in general have long undergone criticisms and complaints from people working and living nearby due to their emissions of odorous air and chemicals and the resulting potential health implications. A National Research Council report (NRC, 2003) stressed the important nature of odor emissions having adverse impacts (e.g., public annoyance, nuisance lawsuits) on the surrounding local community. A significant need was therefore realized for baseline odor emission rates from livestock facilities and identification of the principal chemicals in the annoying odorous air. These emission rates are used as inputs to odor setback models (e.g., Purdue Odor Setback Model; Lim, et al., 2000), which recommend setback distances applicable between facilities and the surrounding neighbors based on odor risk and annoyance. Similarly, chemical emission rates corre-

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sponding to odorous air may be used in comparison with other industries and U.S. Environmental Protection Agency (USEPA) regulations to objectively estimate potential health impacts of livestock facilities.

In 2007, the 24-month National Air Emissions Monitoring Study (NAEMS) study was launched to provide accurate measurements of livestock barn exhaust ventilation rate, gaseous chemical and particulate matter concentrations, and supporting data such as barn temperatures, humidities, and pressures. The barn monitoring portion of the NAEMS investigated these parameters at barns located at 14 confined animal feeding operations (CAFOs) in the egg, broiler, dairy, and swine production industries (Heber et al., 2008; Heber et al., 2011). The overall goal was to establish representative emission rates for livestock production and provide the USEPA with a scientific basis for the implementation of existing air pollution regulations on livestock facilities.

Since the NAEMS was designed first and foremost to provide the USEPA with scientific facts and data regarding air emissions from livestock facilities, details about odor emissions were not included in the NAEMS itself. This was due to the fact that odor nuisance is not addressed by USEPA regulations. Odor nuisance issues are, however, important at the state and local levels of government. Hence, an add-on study to the NAEMS was conducted to measure odor emission rates and identify key odorants associated with CAFOs. This involved collecting a series of odor samples from barn ventilation inlet and outlet locations, similar to the studies reported by Jacobson et al. (2002) and Lim et al. (2004), and simultaneous chemical samples from the same locations. The goals of this study were to:

- Determine odor emission rates using common protocols and standardized olfactometry for use in odor setback and air dispersion models.
- Develop a comprehensive chemical library that delineates the most significant odorants.
- Correlate the observed chemical analysis with olfactometric (sensory) evaluations.

The specific goals for part 1 of this six-article series are to present (1) the sample collection and analysis methods used by the olfactometry and chemical-olfactometry facilities, (2) the interlaboratory comparisons of testing protocols, and (3) a review of quality assurance and control measures. Part 2 focuses on the odor emissions as measured using triangular forced-choice olfactometry (Akdeniz et al., 2012a). Part 3 discusses the volatile organic compound (VOC) concentrations and emissions as measured by gas chromatography-mass spectrometry with olfactometry (GC-MS-O) (Cai et al., 2012). Part 4 describes the correlations between the sensory (olfactometry) and chemical measurements (Akdeniz et al., 2012b), while Part 5 presents correlations between GC-MS-O sensory data and chemical measurements (Zhang et al., 2012). Finally, Part 6 further assesses the results of the study using the relatively new "odor activity value" approach (Parker et al., 2012).

FARM DESCRIPTIONS

Odor and associated trace chemicals were sampled from November 2007 to May 2009 at four of the 14 NAEMS barn sites (WI5B-dairy, IN5B-dairy, IN3B-finishing pigs, and IA4B-sows). The characteristics of these sites are given in table 1, the site layouts and monitoring locations are provided in figure 1, and site-specific details are discussed in the following sections.

WISCONSIN DAIRY (WI5B)

The Wisconsin site was a 1700-cow dairy farm, at which two freestall barns were monitored (barns 1 and 2 with capacities of 275 and 375 Holstein cows, respectively). Barn 1 was located south of barn 2 (fig. 1a). The barns were connected by a covered 29 m long breezeway with curtains on each side. Barn 1 had four rows of stalls, while

Table 1. Barn and management characteristics of NAEMS sites tested for odor and trace chemicals.

	Barns	WI5B	IN5B	IA4B[a]	IN3B[b]
Animal type	-	Dairy	Dairy	Swine	Swine
Barn type	1 and 2 3	Freestall	Freestall	Gestation Farrowing	Finishing
Barn capacity (head)	1 and 2 3	275 and 375	1500 to 1700	1100 24	1000
Bedding/floor type	1 and 2 3	Pine shavings and sand[c]	Digested manure	Slatted Iron/plastic	Slatted
Ventilation type	1 and 2 3	Crossflow	Tunnel	Tunnel Crossflow	Tunnel
Number of wall fans (and number of pit fans)	1 and 2 3	59 and 66	76	11 (9) 2 (1)	4/1 (3)[d]
Fan (and pit fan) diameter (cm)	1 and 2 3	130	140	122 (50 and 61) 61 (25)	122/90 (61)[d]
Barn dimensions (m)	1 and 2 3	93 × 28 and 107 × 30	472 × 29	86 × 25 21.3 × 6.5	61 × 12
Manure removal system	1 and 2 3	Flush and scrape[c]	Scrape	Deep pit Pull plug	Deep pit
Manure removal interval	1 and 2 3	8 h	8 h	180 to 365 d 20-24 d	180 d

[a] Barn 3 at IA4B corresponds to one room in a 16-room farrowing building.
[b] Barns 1 and 2 at IN3B correspond to two rooms in the same 4-room finishing building.
[c] WI5B manure management system was changed from flush to scrape in September 2008.
[d] IN3B had four 122 cm wall fans, one 90 cm wall fan, and three 61 cm pit fans in both barns 1 and 2.

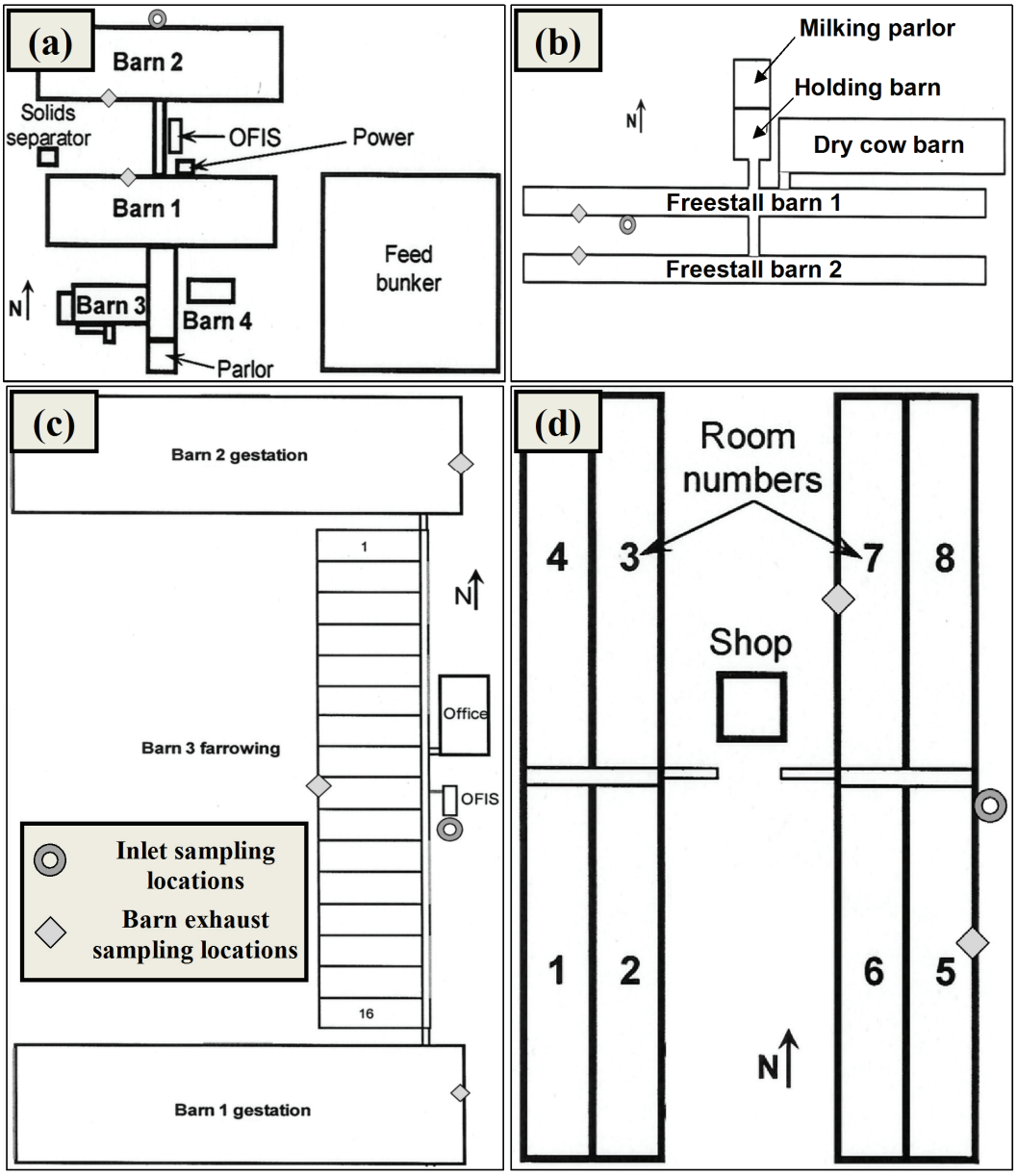

Figure 1. Site layout including monitoring locations for the (a) Wisconsin dairy (WI5B), (b) Indiana dairy (IN5B), (c) Iowa swine (IA4B), and (d) Indiana swine (IN3B) facilities.

barn 2 had five rows. The two barns were ventilated by mechanical cross-ventilation, with fifty-nine 132 cm diameter exhaust fans placed side-by-side along the north wall of barn 1 and sixty-six 132 cm diameter fans along the south wall of barn 2. The opposing walls in the barns were fitted with retractable curtains as well as cooling misters for incoming summertime air. These curtains operated with a minimum opening of 2.5 cm and a maximum opening of 2.0 to 2.5 m. The exhaust fans and the opening of the top 61 cm of the curtains were controlled by barn temperature sensors. Approximately halfway through the study (September 2008), the manure removal system was changed from a flushing system (three times per day, approximately every 8 h) to a tractor scrape system, on approximately the same removal schedule. This change was made in response to the freestall surfaces being switched to sand bedding from wood shavings. Removed manure passed through a solids and/or sand separation unit and was stored in a three-stage manure basin until land application, approximately every six months.

INDIANA DAIRY (IN5B)

The Indiana site was a 3400-cow dairy farm at which two freestall barns were monitored; barn 1 was located 18 m north of barn 2 (fig. 1b). Each barn housed 1500 to 1700 Holstein cows, and individual cows resided for approximately 320 days per year in one of these freestall barns and were otherwise housed in a dry cow barn. The barns had four rows of stalls and were tunnel-ventilated, with seventy-six 137 cm diameter exhaust fans (eight positioned in two rows on each end wall, twelve grouped at the end of each side wall, and six spaced along the freestalls on

each side wall) and adjustable curtains (based on barn temperature) for inlet ventilation air. Both the exhaust fans and side wall summertime cooling cells were controlled based on measurement signals from barn temperature sensors. Manure was removed via a scrape system three times per day, with manure residing in collection gutters inside the barns for about 16 h (approximately two scraping cycles) before it was flushed into an anaerobic digester. Solids were separated from effluent and stored for use as bedding, which was replenished in the barns three times per week, with the remaining liquid transferred into a two-stage storage basin. Gray water was used daily for crop irrigation, and manure was land applied approximately every six months.

IOWA SWINE (IA4B)

The Iowa swine facility (fig. 1c) was a 2500-head sow farm, with three barns (two gestation and one farrowing) monitored during the NAEMS. Each of the gestation barns had a capacity for 1100 breeding/gestation sows, while the farrowing barn held 384 sows among 16 rooms. The two gestation barns were oriented perpendicular to the farrowing barn, which filled the 113 m long separation between the gestation barns. The sow residency time in the gestation barns was approximately 119 days per gestation cycle, whereas sows and litters were kept in the farrowing rooms for 20 to 24 days. Ventilation of the gestation barns was achieved by eleven wall fans (122 cm diameter) and nine pit fans (50 to 61 cm diameter) per barn, with tunnel ventilation in warm weather. Evaporative cooling cells cooled incoming air during hot weather. In cool weather, air was admitted through 30 ceiling inlets, and supplemental heating was provided by six heaters in each barn. The farrowing barn was ventilated by sixteen 25 cm pit fans (one per room) and thirty-two 61 cm wall exhaust fans (two per room). Inlet air entered each room through six ceiling air inlets and four wall inlets from a preheated hallway, and supplemental heat was provided by one heater in each farrowing room. Both gestation barns had concrete slatted floors, with 3.1 m deep pits (each with three pit partitions) underneath that provided about 12 months of storage, after which the pits were emptied. The 61 cm sidewall curtains were opened before agitation of the pits during the pit pumpout process. About 30 to 46 cm of manure was left in the pits after pumpouts occurred. The farrowing barn had a combination iron/plastic/concrete floor with a 61 cm shallow pull-plug pit for short-term manure storage. Manure was swept or scraped into this pit five times per week, and the stored manure transferred to the pit of the nearest gestation barn every 21 to 24 days. Only wastewater from the between-litter room washing process resided in the farrowing pit after a manure transfer.

INDIANA SWINE (IN3B)

The Indiana site was an 8000-head swine finishing facility, at which one of the two 4-room "quad" barns was monitored (fig. 1d). For the purpose of this study, rooms 5 and 7 of this barn (separated by a 3.2 m wide hallway) were treated as the barn 1 and barn 2 sampling locations, respectively. For about the first 110 days of each growing cycle (Jin et al., 2012), all nursery pigs (approximately 4000 head) were housed in two rooms, after which they were separated to fill the other two rooms as growth demanded. The barn was mechanically ventilated year-round using three 61 cm pit fans and one 92 cm and four 122 cm diameter end wall fans (used in stages as barn temperature increased). In cool weather, air was admitted into the room through ceiling inlets. In warm weather, air was admitted through a 12 m long sidewall curtain opening. The sidewall curtain and end wall fans were controlled based on barn temperature, which was monitored by two sensors in each room. Manure management in the barn consisted of concrete slatted floors with a 2.4 m deep pit that was partitioned lengthwise into two distinct pits. Airflow between these pits (through equalizer holes) was completely stopped once the stored manure reached a depth of 15 cm. The manure was pumped out approximately every 180 days for field application.

METHODS

SAMPLING

Odor and chemical samples were collected at each of the four sites approximately every two weeks for 52 weeks over a span of 17 months beginning in November 2007. Four 13-week-long rounds of sampling with six sampling events per round occurred at each site. Additionally, an interlaboratory comparison (IC) sampling event occurred at one of the sites during the 13th week of each round, for a total of 100 sampling events (25 per site).

Odor samples were collected through a stainless-steel positive-pressure bleed valve on a gas sampling system (GSS) available at each NAEMS site (fig. 2). Each GSS included Teflon sampling lines, a diaphragm pump, and Teflon-lined stainless steel pneumatic control solenoids. For most sampling events, a flow-splitting Teflon manifold was also utilized. Chemical samples were pumped through a Teflon line from the analyzer manifold of the GSS. Sampling locations were chosen to represent the background inlet air and the barn ventilation exhaust air. Manual selection of any location sampled by the GSS was facilitated by a computerized data acquisition program (Ni et al., 2009).

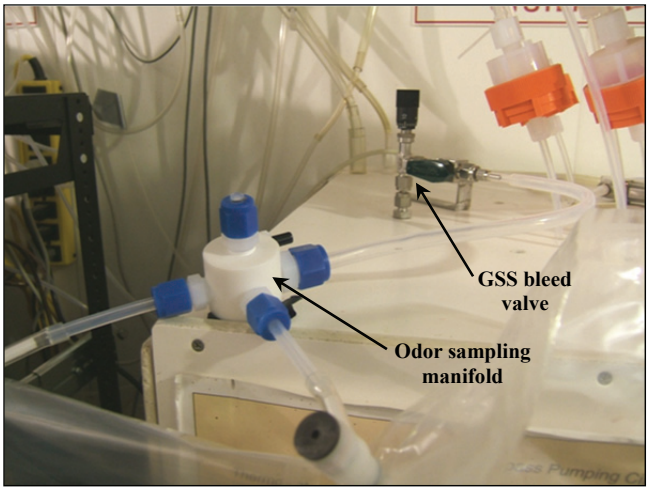

Figure 2. Teflon odor sampling manifold and stainless-steel GSS bleed valve used to collect bagged odor samples (Anderson-Bereznicki, 2009).

The odor samples were collected and transported for analysis via 0.05 mm thick 10 L Tedlar bags with polypropylene fittings. The flow rates of air flowing into the bags were measured with a flow calibrator (Gilibrator-II, Sensidyne, LP, Clearwater, Fla.) before and after sample collection. From these measurements, flow adjustments were made as needed. Chemical samples were collected using sorbent tubes, which were double-passivated, 304-grade stainless steel tubes packed with 65 mg of Tenax TA. Each tube was sampled with a pocket pump (Part No. 210-1002, SKC Inc., Eighty Four, Pa.) at a flow rate of 70 mL min^{-1}. The flow rate was monitored during sample collection with a low-flow bubble meter connected at the tube outlet, in series with the pocket pump.

Each sampling event was comprised of eight odor and four chemical samples collected among the representative inlet and exhaust sampling locations. All samples were collected between 7:00 a.m. and 4:00 p.m. local daylight time (eastern daylight time for IN5B and IN3B, and central daylight time for sites WI5B and IA4B). This allowed characterization of odor and associated chemicals under consistently daytime emission rates to establish variations across seasons, even though the data were insufficient to indicate diurnal patterns of the emissions. Two barns were available for sampling at sites WI5B, IN5B, and IN3B. Hence, duplicate inlet and triplicate barn exhaust odor samples were gathered at these sites. This gave a total of eight samples, consisting of two inlet and six exhaust samples. At site IA4B, the odor samples were gathered across three barns, resulting in duplicate inlet odor samples, duplicate exhaust samples from a farrowing room, and duplicate exhaust samples from each gestation barn. This resulted in a total of two inlet and six exhaust samples. At each site, one chemical sample was taken per sampling location, for a total of three samples at WI5B, IN5B, and IN3B and four samples at IA4B. Sorbent tube samplings occurred during every other odor sample collection, and tubes were drawn simultaneously or in parallel with the odor samples. Hence, related chemical results existed for 50% of the total number of sampling events.

A summary of the collected samples and associated flow rates, collection styles, and sample periods is presented in table 2. During the first six sampling events at each site (i.e., the first round of collection), two sampling regimes (A and B) were followed. Regime A reflected the initially chosen sampling period of 30 min per location, which resulted in odor bag samples of inlet and exhaust air being collected over 15 and 10 min, respectively. Regime B corresponded to the biweekly routine of the sorbent tube collections, and overall sampling periods were restricted to 60 min per location. As a result, the odor bags were sequentially collected over sampling periods twice as long as defined in regime A. Due to minor fluctuations in inlet concentrations, it was anticipated that the longer sampling period of the inlet would have a negligible effect on characterization of inlet concentrations and, therefore, the inlet and barn concentrations were comparable. After the first sampling round, a third sampling regime (C) was employed, with all samples collected over 60 min. This pattern was maintained for the remaining 39 weeks (three rounds) of sample collection. During regime C, each site incorporated a Teflon manifold with the GSS bypass valve connection for improved collection of the sorbent tubes in parallel with the odor sampling. Duplicative or triplicative odor bag samples from a given location were also collected simultaneously (with replication) through a Teflon manifold.

Each 13-week round of sampling was concluded with an IC event. One IC event was conducted for each of the four NAEMS sites. The IC samples were analyzed as a quality control measure for each olfactometry laboratory (see Quality Control and Assurance section). For an IC event, the odor samples were collected into Tedlar bags in triplicate, resulting in a total of six inlet and 18 barn exhaust samples. These samples were divided randomly into three sampling sets comprised of eight odor samples, with two from the inlet location and six from the barn exhaust locations (and with at least one sample per barn). Each set of samples was distributed to one of the three olfactometry laboratories. The first IC sampling event occurred at the Wisconsin dairy (WI5B). The samples were collected in parallel using a four-port Teflon manifold, which was used later in the sampling schedule for all odor samples. However, the limited number of ports on the manifold restricted sampling in parallel, and the samples were drawn as sequential sets of three samples. This resulted in sampling times of 30 min for every three inlet odor samples and 20 min for every three barn exhaust samples, for a total collection time of 1 h per sampling location. During the final three IC events (at IN5B, IN3B, and IA4B), a larger ten-port Teflon manifold was developed by Purdue University and utilized to allow for complete simultaneous measurement of the three sets of odor samples.

OLFACTOMETRY ANALYSIS

Three olfactometry laboratories were involved with the odor evaluations. Sites WI5B, IA4B, and IN5B were evaluated by the University of Minnesota (Jacobson et al., 2008),

Table 2. Characteristics of the three sampling regimes.

Sampling Regime	Sites	Sample Media	Flow Rate (cm^3 min^{-1})	Collection Mode	Sampling Period (min)	Samples per Location (and total)
A	WI5B, IN5B, IN3B	Bags (inlet/barn)	450/660	Sequential	15/10	2/3 (8)
	IA4B	Bags (inlet and barn)	300	Sequential	15	2 (8)
B	WI5B, IN5B IN3B	Bags (inlet/barn)	225/330	Sequential	30/20	2/3 (8)
		Sorbent tubes	70		60	1 (3)
	IA4B	Bags (inlet and barn)	220	Sequential	30	2 (8)
		Sorbent tubes	70		60	1 (4)
C	WI5B, IN5B, IN3B	Bags (inlet/barn)	220/330	Simultaneous	60	2/3 (8)
		Sorbent tubes (every other week)	70		60	1 (3)
	IA4B	Bags (inlet and barn)	100	Simultaneous	60	2 (8)
		Sorbent tubes (every other week)	70		60	1 (4)

Iowa State University (ISU, 2005), and Purdue University (Lim et al., 2004), respectively. Evaluations of IN3B were shared on a biweekly routine between the University of Minnesota and Purdue University.

All collected odor samples were evaluated within 30 h of sample collection using a commercial olfactometer that was common between labs (AC′SCENT international olfactometer, St. Croix Sensory, Lake Elmo, Minn.). This olfactometer was operated in accordance with U.S. (ASTM, 1997) and European (CEN, 2001) standards. The odor assessment procedure included dynamic, triangular, forced-choice olfactometry, with a panel of four or more trained odor assessors providing at least eight single or repeated odor evaluations. Each panel member was qualified through training, sensory screening, and continuous monitoring of their performance according to the European standard (CEN, 2001). The olfactometry assessment process presented three airstreams to each panelist, one at a time. Of the three airstreams, two presented non-odorous carbon-filtered air and one stream was a dilution of activated-carbon-filtered air and a small amount of odorous air taken from the sample bag. The starting dilution level for evaluation was chosen below and incrementally increased to each panelist's detection threshold (DT). A panel's average (geometric mean) of the individual panelists' DTs provided the measure of a sample's odor concentration (odor units per cubic meter, OU m^{-3}) and represented the sample's odor concentration (CEN, 2001). An additional measure, the European odor unit (OU_E), was reported, wherein a panel's average concentration was normalized by the panel mean for a standard mixture of 40 ppm n-butanol in nitrogen, which was determined each session.

In accordance with standards, panelists were screened to determine if their sensitivity to a reference odor (n-butanol) was within the "normal" range of odor response. To ensure that panelists maintained their "normal" sensitivity without excessive variability, the DTs for 40 ppm n-butanol in air were obtained for each lab session and were tracked over time. Each panelist's running average over ten samples was required to remain between 20 and 80 ppb; otherwise, the panelist's results were disqualified. An additional quality assurance strategy for panelists' sensitivity, defined by the CEN standard, required that no sample response be accepted into a data set if the log standard deviation of a panelist's individual DT for the sample varied by more than ±2.3 (McGinley and McGinley, 2006).

Three other quality assurance procedures for odor analyses were utilized. First, while traditional triangular forced-choice olfactometry ceases evaluation once a panelist correctly recognizes the odorous airstream, evaluations were continued until three consecutive correct responses were given. These responses could be any combination of "detect" or "recognize," provided they were consecutively correct identifications of the odorous airstream. This strategy was chosen so that the subjective measurements of odor (intensity, character, hedonic tone) were made at a sufficiently high odor concentration for the panelist to draw definitive qualitative assessments of the odor. A second analysis procedure standardized the hedonic tone scale to -4 to +4, with 0 being neutral, so that all laboratories utilized the same scale. Lastly, mixtures of n-butanol in water were used for evaluating odor intensity, as defined by ASTM Standard E544-99 (ASTM, 2004). The intensity evaluation process was common to all three labs and involved comparison of an odor sample to the static odor intensity referencing scale (table 3; ASTM, 2004).

Table 3. Static odor intensity referencing scale.

Intensity Scale	n-Butanol in Water (ppm)	Odor Intensity Strength
1	250	Very faint
2	750	Faint
3	2250	Moderate
4	6750	Strong
5	20250	Very strong

CHEMICAL ANALYSIS

The Iowa State University laboratory analyzed chemical samples for the following 15 common chemical species: acetic acid, propanoic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, hexanoic acid, phenol, p-cresol, 4-ethylphenol, 2-aminoaceto phenone, indole, skatole (3-methylindole), heptanoic acid, and guaiacol.

All sorbent tubes were conditioned by thermal desorption (260°C for 5 h) with nitrogen at 100 mL min^{-1}, and investigations for cleanliness were made using background chromatograms. For re-used sorbent tubes, sufficient cleanliness was found when preconditioning at 260°C for 30 min was employed. Sorbent tubes were shipped via cooler with ice packs, and temperatures were recorded upon delivery. The chemical samples were analyzed through an ATD inlet (model 3200, Microanalytics, Round Rock, Tex.) for the Agilent 6890 GC and a Microanalytics multidimensional GC-MS-O with olfactometry (GC-MS-O). The general GC run parameters used were as follows: injector, 260°C; FID, 280°C, column, 40°C initial, 3 min hold, 7°C min^{-1}, 220°C final, 10 min hold; carrier gas, GC-grade helium. Odor evaluations were made and results collected from a trained human panelist for the separated VOCs through the GC-MS-O sniff port. Due to the targeting of specific odorants in the samples, chemical and odor evaluations were conducted within two different concentration ranges. For each concentration range, a six-point calibration curve was developed using standard solution mixtures (Zhang et al., 2010).

QUALITY CONTROL AND ASSURANCE

Quality control and assurance measures for both odor and chemical samples were implemented at each collection event. These included:

- Storage of the samples inside the sampling and analysis spaces except during transportation.
- Adjustment periods (15 to 30 min) upon switching to a new sample location to ensure no cross-contamination with other sampling locations.
- Measurement with breakthrough sorbent tubes on one sample per event to monitor for tube saturation, with sampling methods adjusted accordingly.
- Collection of sorbent tube field blanks during each sampling event.

Quality control measures were also implemented at each lab to ensure data reliability and comparability of results among the laboratories. Analysis procedures and sampling protocols were harmonized among the labs and followed standard methods. For example, all olfactometry labs documented panelist sensitivity using 40 ppm n-butanol and collected samples with true replication. In addition, interlaboratory comparison (IC) sampling events were conducted for direct comparison of results and performance from the three olfactometry labs.

INTERLABORATORY OLFACTOMETRY COMPARISON

Olfactometry IC tests were conducted at the end of each 13-week sampling round. Each laboratory evaluated a set of eight collocated samples from one of the four sites. In each IC event, the panel average dilution-to-thresholds (DT) for the eight odor samples and n-butanol standard were compared among labs. Both inter- and intra-laboratory comparisons were made using standard comparative methods (ASTM, 2009). Additional olfactometry results for the normal sampling schedule can be found in the second article in this series (Akdeniz et al., 2012a).

The panels' geometric average DTs for each sample and for each IC event are presented in table 4. The sample numbers correspond to the order (from 1 to 13) under which the samples were taken at each site: WI5B (inlet, barn 1, barn 2), IN5B (inlet, barn 1, barn 2), IN3B (inlet, barn 1, barn 2), and IA4B (inlet, barn 1, barn 2, barn 3). Additionally, the panels' average DT for the n-butanol standard is presented for each IC event. From these data, the reproducibility standard deviation, replication standard deviation, *h* consistency, and *k* consistency statistics were calculated for each sample. As described in ASTM Standard E691-09 (ASTM, 2009; Mandel, 1994), data consistency in the interlaboratory study was evaluated by examining the consistency of a test result between labs (*h* value) and the consistency of within-lab precision between labs (*k* value), as presented in equations 1 and 2, respectively:

$$h = \frac{d}{s_{\bar{X}}} = \frac{(\bar{x} - \bar{\bar{x}})}{\sqrt{\sum_{1}^{P}\left(\frac{(\bar{x} - \bar{\bar{x}})^2}{(p-1)}\right)}} \quad (1)$$

where $\bar{x}$ is the individual-lab average odor concentration across replicate samples, $\bar{\bar{x}}$ is the average of the individual-lab average odor concentrations across labs, and *p* is the number of labs involved in the study (here, *p* = 3).

$$k = \frac{s}{s_r} = \frac{s}{\sqrt{\sum_{1}^{P}\left(\frac{s^2}{p}\right)}} \quad (2)$$

where *s* is the individual-lab standard deviation of odor concentration across replicate samples, and *p* is the number of labs involved in the study (here, *p* = 3).

Hence, all of the IC data were tested against the critical values for *h* and *k* parameters at the 0.5% significance level, as given in ASTM Standard E691-09. For *h* statistics, this critical value was determined from an unpaired t-test based on the number of labs. Similarly, the critical values of *k* statistics were calculated from an F-ratio based on the number of labs and the number of replicates per sample. Due to differences in the number of sample replications per sample, the critical *k* values were 1.72, 1.67, and 1.61 for all inlet and IA4B barn sampling locations (two replications), all other barn exhaust locations (WI5B, IN5B, and IN3B, three replications), and n-butanol samples (four replications), respectively. The *h* parameter was ±1.15 due to participation by three labs. Plots of the *h* and *k* values grouped per lab are given in figure 3, and plots of the *h* and *k* values grouped per sample are presented in figure 4.

As discussed in ASTM Standard E691-09 (ASTM, 2009), laboratory *h* values provide a measure of how each lab performed on a sample-to-sample basis as compared with combined laboratory data. The general pattern of the lab *h* graph (fig. 3, top) indicates that the University of Minnesota lab (UM) tended to have more negatively skewed samples and Purdue's facility (PU) more positive samples, as compared with the combined lab average. The Iowa State University lab (ISU) experienced a large amount of variability across samples as compared with the other two facilities; however, analysis documents did not indicate any observed problems with the analyses performed at ISU. Across facilities, the *h* plot indicates that the number of negative lab samples was approximately equal to the num-

Table 4. Odor concentrations (OU m^{-3}) from the IC events, with replications identified for the three labs as per site, per sample, and for n-butanol at 40 ppm in air.

		WI5B			IN5B			IN3B			IA4B			
Lab[a]	Replicate	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13
UM	1	116	409	229	24	76	44	33	214	179	108	3323	3922	2546
	2	189	414	2023	40	82	51	39	195	179	109	5038	5105	1166
	3	-	-	462	-	82	44	-	253	195	-	-	-	-
	n-butanol	799	-	-	719	-	-	656	-	-	786	-	-	-
PU	1	556	70	303	58	128	128	111	625	525	282	6539	5463	555
	2	76	303	777	53	117	117	103	525	525	219	4146	6539	603
	3	-	189	191	-	117	149	-	525	483	-	-	-	-
	n-butanol	267	-	-	646	-	-	675	-	-	657	-	-	-
ISU	1	1431	34	87	41	1271	61	76	283	347	61	4456	843	349
	2	41	1271	61	34	501	2577	126	283	274	98	5055	2634	391
	3	-	501	2577	-	87	310	-	244	314	-	-	-	-
	n-butanol	310	-	-	1431	-	-	1125	-	-	309	-	-	-

[a] UM = University of Minnesota, PU = Purdue University, and ISU = Iowa State University.

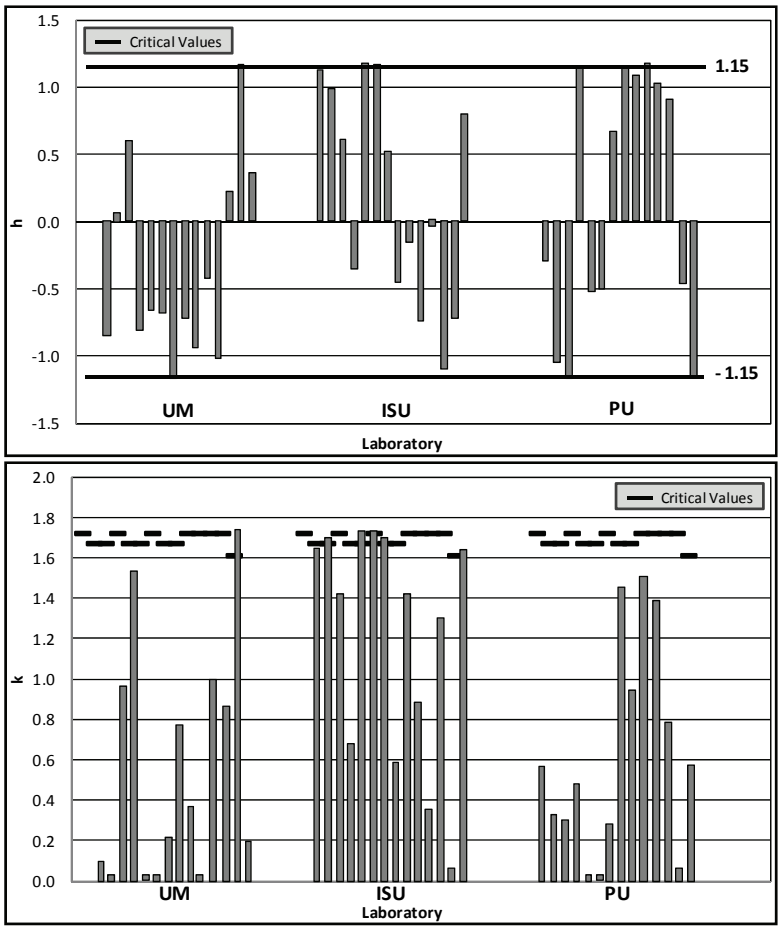

Figure 3. Panel average DT (OU m^{-3}) *h* statistic (top) and *k* statistic (bottom) grouped per lab (left to right: University of Minnesota, Iowa State University, and Purdue University). Critical *k* statistic values change per sample based on the number of replications.

ber of positive lab samples for the entire data set. Collectively, these observations did not indicate any one lab requiring extra investigation and that all labs experienced some degree of expected variability (Mandel, 1994).

Similar to the *h* value analysis, laboratory *k* values provide a measure of the imprecision between replicate samples within a lab. Investigation of the lab *k* values (fig. 3, bottom) indicates that UM had one sample, ISU had five samples, and PU had no samples approaching or exceeding the required threshold value. Additionally, all three labs had a very small number of samples (one to five) approaching zero. While the large variance between samples at ISU was verified, the results of the *k* statistic analysis showed that none of the labs had a majority of their analyzed samples (14 in total) near the zero or critical value. This indicates that each lab performed, individually, with a reasonable amount of variability, and no evidence was provided that the lab procedures were not comparable.

Additional investigations of the lab *h* and *k* values (fig. 4) provided information about individual samples that may need further attention due to discontinuities. While the *h* and *k* values calculated using odor concentrations (OU m^{-3}) highlighted several potential erroneous sample-analysis combinations, the combined results indicate only three samples that were just at or above the associated critical value and in need of further review. These samples corresponded to samples taken from (and analyzed at): IA4B barn 3 (UM), IN5B barn 1 (ISU), and IN5B barn 2 (ISU). Review of field notes from the sample collections did not present marked differences in sample continuity for these particular samples. Similarly, analysis documents did not identify discrepancies in procedures or panelist responses. Hence, these data were retained within the overall set and are considered reliable. A similar sample *h* and *k* value investigation was made using European odor units (OU_E m^{-3}, not presented) to determine the effects of panel sensitivity between the three labs on sample continuity. The analysis showed that both the *h* and *k* values suggested the IN5B barn 1 (ISU analysis) sample evaluation be investigated for sampling or assessment inconsistencies. This may indicate an outlying point or that panelists at ISU responded to barn odors from the IN5B site in an abnormal manner (a concept potentially supported by the lab × sample location interaction reported by Akdeniz, 2010). However, the collection and analysis documentation related to this sample did not indicate obvious discontinuity from other samples and analyses, and hence the data point was retained.

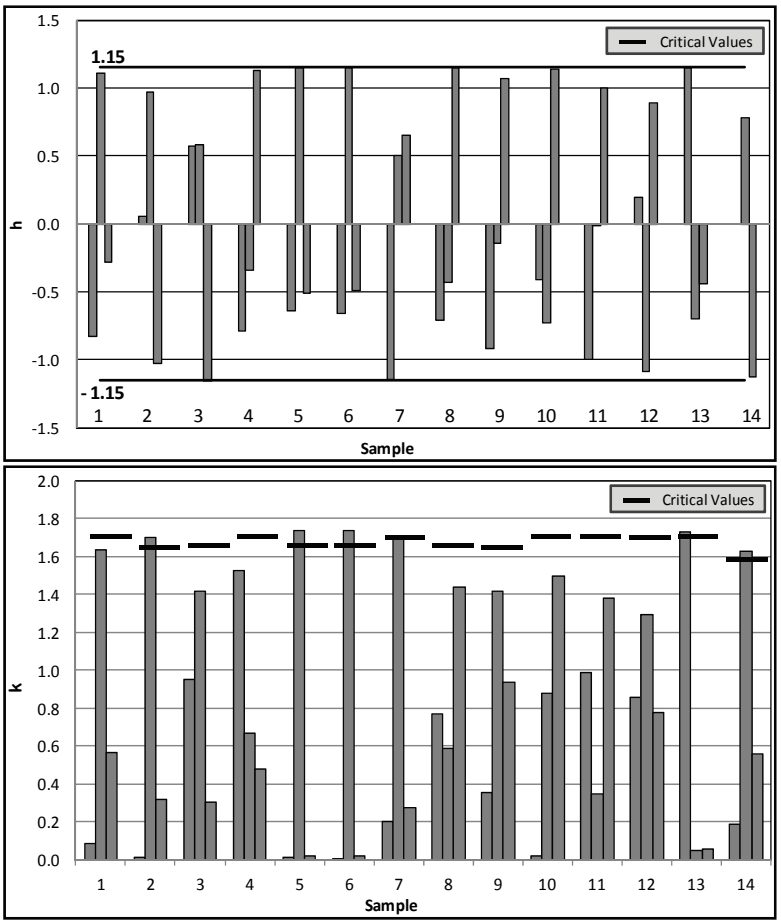

Figure 4. Panel average DT (OU m^{-3}) *h* statistic (top) and *k* statistic (bottom) grouped per sample (1 to 13) and n-butanol (14). Critical *k* statistic values change per sample based on the number of replications.

SUMMARY

From November 2007 to April 2009, 100 odor and chemical sampling events occurred at four of the 14 National Air Emissions Monitoring Study sites: WI5B, IN5B, IN3B, and IA4B. These represented two freestall dairies, one swine finishing site, and one sow farm. Each sampling event involved a series of eight odor and three chemical samples collected with a novel computer-controlled gas sampling system (GSS). The odor samples were collected into Tedlar bags, while sorbent tubes were used to collect odor-associated organic chemicals. Analyses of these samples were facilitated by one chemical and three olfactometry labs associated with the University of Minnesota, Iowa State University, and Purdue University.

A main focus of this study was to achieve continuous laboratory comparability and quality assurance by using a uniform set of sampling procedures for all four livestock facilities. This included collection of odor and chemical samples with replication, taking comparable chemical samples on a biweekly schedule over 52 weeks, collecting three sets of odor samples every 13 weeks for interlaboratory olfactometry comparisons, and ensuring that the odor samples were evaluated within 30 h of collection. In addition to the sample collection process, the olfactometry lab analysis procedures were also standardized. These methods were founded primarily on the basis of internationally accepted panel selection and monitoring principles, but also consisted of evaluations of odor intensity and hedonic tone at the third correct response (either detect or recognition).

Evaluations of panel responses were made for each individual olfactometry lab following standard comparative methods. These results showed a reasonable amount of variability between and within each of the three labs. Per-sample statistical comparisons were also made for two measures of odor concentrations (OU m^{-3} and OU_E m^{-3}) to determine the amount of variability between the labs due to individual panel sensitivities. Of 42 total comparable odor samples, only one was highlighted for additional investigation from the *h* and *k* critical value analyses at 0.5% significance for both the OU m^{-3} and OU_E m^{-3} calculated parameters. This demonstrates that variability between and within labs due to panel sensitivity should be generally considered inherent, with large panel-related variability possible (but inconclusive) for one sample. The interlaboratory tests lend further support to previously reported statistical evaluations suggesting a slight interaction between lab and sample location. Overall, it was determined that the sampling and analysis procedures presented here were comparable between the three labs, and all data reviewed herein were considered reliable at a 0.5% level of statistical significance.

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REFERENCES

Akdeniz, N., L. D. Jacobson, B. P. Hetchler, A. Rendahl, S. D. Bereznicki, A. J. Heber, R. B. Jacko, K. Y. Heathcote, S. J. Hoff, J. A. Koziel, L. Cai, D. B. Parker, and E. A. Caraway. 2010. Odor and odorous chemical emissions from animal buildings: Part 2. Odor emissions. ASABE Paper No. 711P0510cd. St. Joseph, Mich.: ASABE.

Akdeniz, N., L. D. Jacobson, B. P. Hetchler, S. D. Bereznicki, A. J. Heber, J. A. Koziel, L. Cai, S. Zhang, and D. B. Parker. 2012a. Odor and odorous chemical emissions from animal buildings: Part 2. Odor emissions. *Trans. ASABE* 55(6): 2335-2345.

Akdeniz, N., L. D. Jacobson, B. P. Hetchler, S. D. Bereznicki, A. J. Heber, J. A. Koziel, L. Cai, S. Zhang, and D. B. Parker. 2012b. Odor and odorous chemical emissions from animal buildings: Part 4. Correlations between sensory and chemical measurements. *Trans. ASABE* 55(6): 2347-2356.

Anderson-Bereznicki, S. D. 2009. Development of a multiple-source odor setback model for livestock production systems. PhD diss. West Lafayette, Ind.: Purdue University.

ASTM. 1997. E679-91: Standard practice for determination of odor and taste thresholds by a forced-choice ascending concentration series method of limit. West Conshohocken, Pa.: ASTM International.

ASTM. 2004. E544-99: Standard practices for referencing suprathreshold odor intensity. West Conshohocken, Pa.: ASTM International.

ASTM. 2009. E691-09: Standard practice for conducting an interlaboratory study to determine the precision of a test method. West Conshohocken, Pa.: ASTM International.

Cai, L., J. A. Koziel, S. Zhang, E. L. Cortus, D. B. Parker, S. J. Hoff, G. Sun, K. Y. Heathcote, L. D. Jacobson, N. Akdeniz, B. P. Hetchler, S. D. Bereznicki, A. J. Heber, E. A. Caraway, and T. T. Lim. 2012. Odor and odorous chemical emissions from animal buildings: Part 3. Chemical emissions. *Trans. ASABE* (in review).

CEN. 2001. *Air Quality: Determination of Odour Concentration by Dynamic Olfactometry.* Brussels, Belgium: European Committee for Standardization (CEN).

Heber, A. J., B. W. Bogan, J.-Q. Ni, T. T. Lim, E. L. Cortus, J. C. Ramirez-Dorronsoro, C. A. Diehl, S. M. Hanni, C. Xiao, K. D. Casey, C. A. Gooch, L. D. Jacobson, J. A. Koziel, F. M. Mitloehner, P. M. Ndegwa, W. P. Robarge, L. Wang, and R. Zhang. 2008. The National Air Emissions Monitoring Study: Overview of barn sources. Paper presented at the 8th International Livestock Environment Symposium. ASABE Publication No. 701P0408. St. Joseph, Mich.: ASABE.

Heber, A. J., J.-Q. Ni, E. L. Cortus, T. T. Lim, and B. W. Bogan. 2011. National study of livestock air quality in USA. *Proc. Intl. Symp. on Health Environment and Animal Welfare* (ISHEAW-2011), 42-66. Beijing, China: Chinese Society of Agricultural Engineering.

ISU. 2005. Iowa State University Olfactometry Lab website. Ames, Iowa: Iowa State University. Available at: www.abe.iastate.edu/research/facilities/olfactometry-lab.html. Accessed 29 December 2010.

Jacobson, L. D., R. E. Nicolai, A. J. Heber, J.-Q. Ni, T. T. Lim, J. A. Koziel, S. J. Hoff, Y. Zhang, and D. B. Beasley. 2002. Quality assured measurements of animal building emissions: Part 3. Odor concentrations. In *Proc. Symp. on Air Quality Measurement Methods and Technology*. Pittsburgh, Pa.: Air and Waste Management Association.

Jacobson, L. D., B. P. Hetchler, D. R. Schmidt, R. E. Nicolai, A. J. Heber, J.-Q. Ni, S. J. Hoff, J. A. Koziel, D. B. Parker, Y. Zhang, and D. B. Beasley. 2008. Quality assured measurements of animal building emissions: Part 3. Odor concentrations. *J. Air and Waste Mgmt. Assoc.* 58(6): 806-811.

Jin, Y., T. T. Lim, J.-Q. Ni, J.-H. Ha, and A. J. Heber. 2012. Emissions monitoring at a deep-pit swine finishing facility: Research methods and system performance. *J. Air and Waste Mgmt. Assoc.* (in press, doi: 10.1080/10962247.2012.707163).

Lim, T. T., A. J. Heber, J.-Q. Ni, R. A. Grant, and A. L. Sutton. 2000. Odor impact distance guideline for swine production systems. In *Proc. Specialty Conf.: Odors and VOC Emissions*. Alexandria, Va.: Water Environment Federation.

Lim, T. T., A. J. Heber, J.-Q. Ni, D. Kendall, and B. T. Richert. 2004. Effects of manure removal strategies on odor and gas emission from swine finishing. *Trans. ASAE* 47(6): 2041-2050.

Mandel, J. 1994. Analyzing interlaboratory data according to ASTM Standard E691. In *Quality and Statistics: Total Quality Management*. ASTM STP 1209. Philadelphia, Pa.: American Society for Testing and Materials.

McGinley, C. M., and M. A. McGinley. 2006. An odor index scale for policy and decision making using ambient and source odor concentrations. In *Proc. Specialty Conference: Odors and Air Emissions.* Alexandria, Va.: Water Environment Federation.

Ni, J.-Q., A. J. Heber, M. J. Darr, T. T. Lim, C. A. Diehl, and B. W. Bogan. 2009. Air quality monitoring and on-site computer systems for livestock and poultry environment studies. *Trans. ASABE* 52(3): 937-947.

NRC. 2003. Air emissions from animal feeding operations: Current knowledge, future needs. Washington, D.C.: National Research Council.

Parker, D. B., J. A. Koziel, L. Cai, L. D. Jacobson, N. Akdeniz, S. D. Bereznicki, T. T. Lim, E. A. Caraway, S. Zhang, S. J. Hoff, A. J. Heber, K. Y. Heathcote, and B. P. Hetchler. 2012. Odor and odorous chemical emissions from animal buildings: Part 6. Odor activity value. *Trans. ASABE* 55(6): 2357-2368.

Zhang, S., L. Cai, J. A. Koziel, S. J. Hoff, C. Clanton, D. R. Schmidt, L. D. Jacobson, D. B. Parker, and A. J. Heber. 2010. Field air sampling and simultaneous chemical and sensory analysis of livestock odorants with sorbent tubes and GC-MS/olfactometry. *Sensors and Actuators B* 146(2): 427-432.

Zhang, S., L. Cai, J. A. Koziel, S. J. Hoff, K. Y. Heathcote, L. Chen, L. D. Jacobson, N. Akdeniz, B. P. Hetchler, D. B. Parker, E. A. Caraway, A. J. Heber, and S. D. Bereznicki. 2012. Odor and odorous chemical emissions from animal buildings: Part 5. Correlations between odor intensities and chemical concentrations (GC-MS-O). *Trans. ASABE* (in review).